

## Final Report

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This is a report of the results obtained and the accomplishments during the performance period of above grant.

### **Enstatite meteorites and the original heterogeneity of $^{53}\text{Mn}$ distribution in the solar nebula.**

We have shown earlier that the relative abundance of radiogenic  $^{53}\text{Cr}$  in bulk ordinary chondrites ( $\sim 0.48\epsilon$ ) is clearly different from that in the earth-moon system ( $0\epsilon$ ). The SNC parent body (Mars) is characterized by an intermediate  $^{53}\text{Cr}$  excess ( $\sim 0.23\epsilon$ ). We have also shown that the Mn-Cr systematics of the howardite-eucrite-diogenite parent body (HED PB, the asteroid Vesta) is consistent with the chondritic Mn/Cr ratio in the bulk HED PB and that it has a  $^{53}\text{Cr}$  excess of  $\sim 0.5\epsilon$  units which is within error the same as that of chondrites. It appears that the excesses of  $^{53}\text{Cr}$  in these planets are a function of their present heliocentric distance. The study of some other meteorite classes (angrites, pallasites, primitive achondrites) has shown that their Mn-Cr systematics is consistent with that of the ordinary chondrites. The observed gradient in the radiogenic  $^{53}\text{Cr}$  abundances can be explained by a) an early volatility controlled radial Mn/Cr fractionation in the nebula or b) an original heterogeneity of  $^{53}\text{Mn}$ . The first assumption, however, requires the Mn/Cr ratios of the bulk Earth and Mars to be considerably lower than the inferred model Mn/Cr ratios for these two planets. For this reason, we suggested that the observed gradient is due to an original radial  $^{53}\text{Mn}$  heterogeneity in the late nebula.

Much effort during the grant period was devoted to the verification of this hypothesis with the study of the enstatite chondrites. The importance of the enstatite chondrites is that they are potential constituents of the inner planets and that they are highly reduced and, therefore, were proposed to originate at a distance much closer to the Sun than all other meteorite classes. If the latter is true and if our hypothesis on the radial heterogeneity of  $^{53}\text{Mn}$  is correct, the bulk enstatite chondrites should reveal  $^{53}\text{Cr}$  excesses which are smaller than in the other meteorites if their parent bodies had a chondritic Mn/Cr ratio. Our earlier results for the EH4-chondrite Indarch has shown that this is indeed the case: the  $^{53}\text{Cr}$  excess ( $\sim 0.17\epsilon$ ) for bulk Indarch clearly deviates from that of the ordinary chondrites ( $\sim 0.48\epsilon$ ) while its Mn/Cr ratio is essentially chondritic. To confirm this first result and to extend the Mn-Cr systematics to the other type of enstatites - EL-chondrites, we studied the EH-chondrite -Abee - and the EL-chondrite Khairpur. To obtain phases with different Mn/Cr ratios we have utilized a differential dissolution procedure similar to that which was successfully used for Indarch. We have measured the isotopic composition of Cr and Mn and Cr concentrations in the leaches, residue, and in the large (1-1.5 g) bulk samples of Abee and Khairpur.

Abee. The Abee data yield a  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of  $(3.0 \pm 0.6) \times 10^{-6}$  with an initial  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio of  $-0.03 \pm 0.11\varepsilon$  at the time of isotope closure. These values are indistinguishable within uncertainties from those of Indarch ( $(2.8 \pm 0.2) \times 10^{-6}$  and  $-0.04 \pm 0.05$ ). This indicates that the Mn-Cr isotope system closed in these two meteorites essentially contemporaneously. The Mn/Cr ratio in the studied bulk sample is much lower than that in Indarch and ordinary chondrites. However, Abee is a notoriously heterogeneous meteorite and the Mn/Cr ratios vary from sample to sample. The average Mn/Cr ratio which we calculate from the literature data is close to chondritic. We note that at the chondritic Mn/Cr ratio the  $^{53}\text{Cr}$  excess is the same as that of Indarch ( $\sim 0.17\varepsilon$ ) and that the Abee isochron also passes clearly below the bulk ordinary chondrite data point. Thus, the results for the two EH-chondrites are consistent and indicate that the  $^{53}\text{Cr}$  excesses in the bulk EH-chondrites are clearly lower than those in the bulk ordinary chondrites while the Mn/Cr ratios are essentially the same.

Khairpur. The data points for the leaches, residue, and total rock also form a well defined correlation line whose slope yields a lower  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio as compared to the EH-chondrites:  $(1.22 \pm 0.07) \times 10^{-6}$ . The most important feature here is that, again, the line passes below the bulk ordinary chondrites and the  $^{53}\text{Cr}$  excess at the chondritic Mn/Cr ratio ( $\sim 0.15\varepsilon$ ) is similar to that of the EH-chondrites.

Thus, the essential peculiarity of all three studied enstatite chondrites is that their isochrons pass distinctly below the ordinary chondrite data point: the  $^{53}\text{Cr}$  excesses in the E-chondrites at the  $^{55}\text{Mn}/^{52}\text{Cr}$  ratio of 0.76 are 0.15-0.17  $\varepsilon$ , in contrast to that in the ordinary chondrites and the other "asteroid belt" bodies. We do not see any other reasonable explanation for this difference except the heterogeneity in original  $^{53}\text{Mn}$  abundance: because the Mn/Cr ratios in bulk ordinary chondrites and in bulk enstatite chondrites are the same this difference cannot be explained by an early Mn/Cr fractionation.

In summary we conclude, that the obtained results on the E-chondrites indicate that *the original  $^{53}\text{Mn}$  distribution in the nebula was heterogeneous.*

Place of origin of the E-chondrites. From the bulk E-chondrites  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio of  $\sim 0.16\varepsilon$  and the observed correlation between the  $^{53}\text{Cr}$  excesses vs. heliocentric distance it follows that the E chondrite parent bodies have originated at distances around 1.4 AU. This implies that E-chondrite material was formed near there and some of the planetesimals were subsequently transported to the asteroid belt where the meteorites now come from. If, however, the Mn/Cr of the bulk Earth was somewhat lower than chondritic as some researches believe (this would imply that the dependence between the  $^{53}\text{Cr}$  excesses vs. heliocentric distance is not linear), the place of origin would be even closer to the Earth's orbit. The Cr isotopic signature of the E-chondrites is consistent with the assumption that E-chondrite type material contributed to the formation of the inner planets.

Chronology of the E-chondrites. Because the original abundances of  $^{53}\text{Mn}$  in the EH- and EL-chondrites were the same, the relative  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age of Khairpur can be calculated by the direct comparison of its  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio with that of Indarch. This comparison indicates that the EL6-chondrite Khairpur is  $\sim 4.5$  Ma younger than the EH4-chondrites Indarch and Abee. These results are in good agreement with the  $^{129}\text{I}$ - $^{129}\text{Xe}$  data which yield  $\sim 4$  Ma difference between the EH-chondrites and Khairpur (Kennedy B.M.,

Hudson B., Hohenberg C.M., and Podosek F.A., 1988). The younger  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age of this meteorite with a higher metamorphic grade may represent a cooling age.

Although the original  $^{53}\text{Mn}$  abundance in the E-chondrites was different from that of the other meteorites and, therefore, the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age cannot be obtained in a straightforward way (that is, by comparing their  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios with that of the angrite LEW86010, as we have done for 'chondritic Mn/Cr' meteorites), it is possible to deduce the relationship between their original  $^{53}\text{Mn}$  abundances:  $(^{53}\text{Mn}/^{55}\text{Mn})_{0, \text{ E-chon.}} = (^{53}\text{Mn}/^{55}\text{Mn})_{0, \text{ Ord. Chon.}} - 4.7 \times 10^{-6}$ . Using the lower and the upper limits for the solar system age of 4568 and 4571 Ma and the corresponding  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios, as inferred by us earlier, we obtain absolute  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  ages of Indarch and Abee of 4564-4566 Ma. These old ages clearly show that the EH-chondrite parent body formed at the very early accretionary stage of the solar system.

### **Martian meteorites.**

We have shown earlier that samples from Martian meteorites ALH84001 (ALH) and Shergotty (SHE) have the same  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios of 0.22-0.23 $\epsilon$  which appears to be characteristic for Mars. The subsequent study of the Martian meteorite EETA79001 (EETA) has yielded a  $^{53}\text{Cr}$  excess of  $\sim 0.27\epsilon$  which seems to be only marginally but in all measurements consistently higher. If this hint is true then the EETA source must have separated from the Mars mantle earlier than that of ALH and SHE. This would be consistent with the fact that EETA has a clear excess of  $^{182}\text{W}$  (the decay product of  $^{182}\text{Hf}$ ;  $T_{1/2}=9$  Ma) of  $\sim 2\epsilon$  while the  $^{182}\text{W}/^{184}\text{W}$  ratios in ALH and SHE are indistinguishable from chondritic (Lee D.-C. and Halliday A.N., 1997). In an attempt to resolve these tiny differences in the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios we conducted in the past year a series of measurements of the Nakhla meteorite which is also characterized by an elevated  $^{182}\text{W}/^{184}\text{W}$  ratio of  $\sim 3\epsilon$ . Our preliminary results have shown that the  $^{53}\text{Cr}$  excess in Nakhla is also slightly higher than those of ALH and SHE:  $\sim 0.26\epsilon$ . Because these differences are very small we have to accumulate much more statistics to ascertain that they are real and that they can be used to constrain the early evolution of Mars.

### **The $^{53}\text{Mn}$ - $^{53}\text{Cr}$ system as a tracer for extraterrestrial material on Earth.**

K/T boundary. The observed difference in the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios between Earth and the other solar system objects motivated us to use the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratio as a tracer for cosmic material on Earth. We completed in this grant period a series of measurements of sediments from the Cretaceous-Tertiary (K/T) boundary layer. One of the long-standing problems in the studies of the K/T event was the distinction between the two alternatives: cosmic (asteroid impact) or terrestrial (volcanism) cause of the observed phenomena. Although several lines of evidence in favor of the cosmic origin of the K/T event have been found, direct (isotopic) evidence was still missing. To confirm isotopically the presence of the cosmic material in the K/T sediments we have measured the Cr isotopic composition of the K/T boundary samples FC10 and SK10 from Stevns Klint, Denmark, of SM503 from Caravaca, Spain, and of two background samples below and above the K/T boundary. The  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios of the background clays are indistinguishable from other terrestrial samples while those of FC10, SK10, and SM503 ( $-0.33 \pm 0.04\epsilon$ ,  $-0.35 \pm 0.04\epsilon$ , and  $-0.40 \pm 0.04\epsilon$ , respectively) are different from that of Earth and indicate

that much of the Cr must clearly be of extraterrestrial origin. The Cr isotopic signature of the K/T samples is very similar to that of the carbonaceous chondrites (the apparent deficit of  $^{53}\text{Cr}$  is actually due to an elevated  $^{54}\text{Cr}/^{52}\text{Cr}$  ratio and the application of a second order fractionation correction). Thus, we consider this finding as first isotopic evidence for the presence of a cosmic component in the K/T boundary. Moreover, the Cr measured isotopic composition indicates that the impactor was of a carbonaceous chondrite type material.

### **Publications**

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